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(54) "Fibre – reinforced thermoplastic laminate

(57) A fibre reinforced thermoplastics laminate comprising two or more reinforcing layers, each comprising a first thermoplastics material containing reinforcing fibres, and, disposed between adjacent reinforcing layers, a thermoplastics layer comprising a second thermoplastics material wherein the first and second thermoplastics materials are the same or different and wherein the ratio of the thickness of the thermoplastics layer to each of the adjacent reinforcing layers in between 9:1 to 1:4.5. When molten, the viscosity of the first thermoplastics material is preferably higher than that of the second thermoplastics material. Each thermoplastics layer preferably contains 2% to 20% by volume of short fibres (especially glass fibres). Each reinforcing layer preferably contains carbon or aromatic polyamide fibres which are systermatically aligned in the form of (for example) woven or knitted cloth.

One use of the present laminates is in the manufacture of curved or other non-planar articles by rapid hot compression moulding techniques.

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SPECIFICATION

Fibre reinforced thermoplastics laminates

The present invention relates to fibre reinforced thermoplastics laminates suitable, in particular, for cutting and shaping into non-planar articles.

It is known to produce heavily reinforced laminated structural material by stacking alternate layers of thin thermoplastic films and reinforcing fibre sheets and then subjecting the stack to heat to melt the thermoplastic and bond the layers together. This method, known as film stacking, is described and claimed in, for example, UK Patent No 1485586, where the thermoplastics material is a polycarbonate or a polysulphone.

While such film-stack methods produce laminates of very high fibre loading and hence high strength, particularly if sheets of systematically - aligned high strength fibres are used (eg woven carbon fibre cloth), the laminates produced cannot usually be compression-moulded into curved (or other non-planar) articles without the fibre layers buckling or tearing under the influence of the pressing load. Heating the laminate to soften or melt its thermoplastics content makes deformation by pressing considerably easier. However even under these conditions only a very slow application of pressure on the hot laminate can be tolerated before the laminate buckles. Long mould cycle times are therefore necessary, typically in excess of 10 minutes depending on the degree of laminate distortion required by the mould. This means that the process is energy intensive since it is always essential to heat the mould to the softening point of the thermoplastics during pressing to prevent the thermoplastic material or materials solidifying before laminate deformation has been completed.

It is one object of the present invention to provide a novel fibre-reinforced thermoplastics laminate which may be moulded into the shape of an article at a considerably faster rate than the materials described above. Other objects and advantages of the present invention will become evident from the following detailed description thereof.

Accordingly, the present invention provides a fibre reinforced thermoplastics laminate comprising two or more reinforcing layers, each layer comprising a first thermoplastics material containing reinforcing fibres and, disposed between adjacent reinforcing layers, a thermoplastics layer comprising a second thermoplastics material wherein the first and second thermoplastics materials are the same or different and further wherein the ratio of the thickness of the thermoplastics layer to the thickness of each of the adjacent reinforcing layers is between 9:1 and 1:4.5. The ratio given above refers to the relative thickness of the thermoplastics to the reinforcing layers after the layers have been bonded together.

The present inventors have found that when a fibre reinforced thermoplastics laminate is heated until its thermoplastics content is molten or semi molten (ie above the softening point of both thermoplastics materials) and is subsequently subjected to a deforming load, its resistance against buckling increases as the value of $(d_1d_2)^{1/2}$ increases, where d_1 is the thickness of each of two adjacent reinforcing layers and d_2 is the thickness of the thermoplastics layer between them. Therefore, for a required thickness of laminate ply (ie the thickness of two adjacent reinforcing layers and the thermoplastics layer between them, $(d_2 2d_1)$) the ratio of d_2 to d_1 should be between 9:1 and 1:4.5, and is preferably between 3:1 and 4:3. This compares with a typical d_2 to d ratio in known heavily fibre reinforced thermoplastics laminates of 1:50. Thereby, hot compression moulding cycle times of curved articles made from the present laminates may typically be as low as 15 to 30 seconds, which is comparable to the manufacturing cycle times of much lower strength thermoplastic articles made, for example, by injection moulding.

The present inventors have also found that the resistance against buckling also increases as the value of $(Z_1/Z_2)^{1/2}$ increases where Z_2 is the viscosity of the thermoplastics layers and Z_1 is the viscosity of each of its adjacent reinforcing layers. Preferably, therefore, the first and second thermoplastics materials are different and are chosen such that, above the softening point of both materials and within a temperature range at which both materials exhibit fluid properties, at any one temperature within that range the viscosity of the first thermoplastics material is greater than the viscosity of the second thermoplastics material.

The reinforcing fibres are preferably systematically aligned in the reinforcing layers for maximum strength, that is to say they may be aligned in each layer in the form of, for example, one or more triangulated nets, cross-ply mats (such as woven or knitted cloth), continuous unidirectional mats or discontinuous unidirectional mats. Such fibre alignment forms are more fully discussed and explained by K D Potter (""Deformation mechanisms of fibre reinforcements and their influence on the fabrication of complex structural parts". Proceedings of the Third International Conference on Composites, Paris August 1980). Similarly, for maximum strength each of the reinforcing layers advantageously contains a high volume content of reinforcing fibres, preferably from 40 to 65% by volume.

In order to ensure that the layers of reinforced fibres remain separated from one another during the manufacture of the present laminates and during any subsequent compression moulding it has been found preferable to include up to 30% by volume, and most preferably from 2% to 15% by volume, of short fibres in the thermoplastics layer.

The presence of short fibres imparts to the thermoplastics layer a certin thixotrophic quality and resilience which prevents the adjacent reinforcing layers from collapsing against one another during high temperature pressing operations. Therefore, by preventing the formation of areas of laminate where d_2 approaches zero, localised buckling and tearing of reinforcing layers is discouraged when the laminate is subjected to shear forces during hot compression moulding into curved or other

non-planar articles. However, as laminate resistance against buckling is also found to increase as the value of $(Z_1/Z_2)^{1/2}$ increases, then it is important to ensure that the fibre content of the thermoplastics layer does not increase the layer's viscosity to an unacceptable level. Maintaining a low thermoplastics layer viscosity whilst deforming the present laminate allows the molten or semi-molten second thermoplastic material to flow parallel to the adjacent reinforcing layers and thus allows the laminate as a whole to yield rapidly to the deforming load. Preferably therefore, the thermoplastics layer contains less than 30% by volume and most preferably less than 15% by volume of short fibres.

The length of the short fibres are advantageously less than d_2 to prevent the short fibres from becoming trapped between adjacent reinforcing layers and so restricting the flow of the second thermoplastics material whilst deforming the present laminates. Conveniently, the short fibres are on average between 0.1 and 1.0mm long. The short fibres are preferably randomly aligned in and evenly dispersed throughout each of the thermoplastics layers. The fibres used in the reinforcing layers and the short fibres used in the one or more thermoplastics layers of the present laminate may comprise the same or different materials and may be any of those used conventionally in the production of fibre reinforced plastics. For example, they may consist of or contain carbon fibres, glass fibres, asbestos fibres or aramid fibres. However, because the main function of the short fibres is to hold adjacent reinforcing layers apart while laminate deformation is taking place, rather than to impart strength to the laminate as a whole once solidified, the short fibres need not comprise high strength, expensive materials such as carbon fibre or aramid fibre, nor need they be aligned in the plane of the laminate by a high cost fibre alignment process.

Thermoplastics materials suitable for use in the present laminates include cellulose accetate, cellulose acetate-butyrate, ethyl cellulose, polystyrene, vinylchloride/vinylacetate copolymer, polypropylene, phenoxy polypropylene, polyethylene, polyethylene terephthalate, polybutylene terephthalate, polycarbonate, polyamides (ie nylons), polyesters, polysulphones, polyethersulphones, polyphenylene sulphide, polyimides, and poly-ether-ketone (PEEK). Such materials may conveniently be used for both the second thermoplastics material in the one or more thermoplastics layers and the first thermoplastics material in the reinforcing layers. In the present laminate, the same or different thermoplastics material may be used in adjacent reinforcing layers, and similarly the same or different thermoplastics material may be used in adjacent thermoplastic layers (where two or more such layers are present in the laminate).

It is contemplated that normally the outer layers of the present laminate will be of a third thermoplastics material which may be the same as or different to either of the first and second thermoplastics materials. These final decorative or protective outer layers may be of any desired thickness and may or may not contain short fibres.

One method of manufacturing the present laminates comprises interleaving sheets of first thermoplastic material, second thermoplastic material (optionally containing short fibres), and re-inforcing fibres in an alternating order appropriate to the manufacture of the present laminate, heating the interleaved sheets to at least soften the thermoplastics materials, and then compressing the interleaved sheet for a period of time until all the sheets become bonded together. Where the first and second thermoplastics materials are different, it is important that they are selected to be compatible ie they must sofen and melt at similar temperatures, and they must bond together when subjected to heat and pressure. Alternatively, the sheets of reinforcing fibres may be partly or fully impregnated with the first thermoplastics material prior to stacking, in which case it may only be necessary to interleave sheets of impregnated reinforcing fibres and second thermoplastics material before heating and compressing. In either case, the heat and pressure may be removed once the sheets are fully bonded together and the laminate thus formed allowed to cool. When required outer layers of the third thermoplastics material may be bonded to the laminate during its formation or at a later stage.

The main advantage of the present laminates is that they are suitable for the fast mass production of curved and other non-planar articles by hot press forming operations. These articles may be manufactured by cutting out blanks from the laminate to the appropriate size, heating blanks to soften or melt the thermoplastics materials, placing each hot blank in a mould, closing the mould under pressure, and re-opening the mould when the formed blank is sufficiently cool for its thermoplastics content to have resolidified. By carefully preselecting the thickness of the laminate, the blank may be cut slightly shorter in length and breadth than the finished article such that it fits easily into the mould whilst its volume equals that of the finished article, so that the mould is completely filled once it is closed without excess thermoplastics materials being squeezed out. Mould forming times will generally be very rapid, typically less than 30 seconds. In some cases this means that little or no mould heating is required to prevent premature solidification of the laminate before forming is complete. Generally, however, mould heating to the extent required by typical thermoplastic injection moulding processes is desirable, but this heating is far less than that required for deforming known thermoplastic laminates, where it is important to maintain the temperature of the mould at or near the thermoplastics softening point temperature throughout the relatively much longer period of deformation. The presence of one or more thick thermoplastics layers in the laminate means that the laminate can accommodate relatively large variations in article thickness whilst still retaining the same degree of reinforcement throughout. Furthermore, compression moulding tends to squeeze some of the second thermoplastics materials out of

the thick thermoplastics layer or layers around the edges of the slightly undersized blank, thus ensuring that the edge details of the finished articles are well defined. The addition incorporation of thermoplastic outer layers on the laminate provides a means of ensuring that the surface details of the articles are also well defined.

An embodiment of the present invention will now be described by way of example only.

A reinforcing layer precursor was first prepared by stacking three sheets of nylon 6 film interleaved with two sheets of 5 shaft satin carbon fibre cloth. Two such precursors were stacked one on top of the other, and between them was inserted a 1.2 mm thick consolidated layer of a glass fibre-filled nylon 6.6 moulding compound containing 15% by volume glass fibres of average length 0.2 mm, average diameter 10 microns. The complete assembly was placed in a flat mould, preheated to 350°C. After one minute a pressure of 2-3 Mpa was applied and maintained over 10 minutes. The mould was allowed to cool to 150°C, and the resulting solidified and fully bonded laminate was removed. Upon examination, each of the outer precursors was found to have consolidated into a solid continuous layer 0.6 mm thick containing 50% by volume carbon fibre and the remainder nylon 6. Once cooled, the resultant laminate was found to have an average flexural modulus of 40 GPa and an ultimate flexural strength of 420 MPa.

Two methods of producing a 1000 cm^2 non-planar article from the above three-ply laminate are as follows:

1. A blank was first cut from the laminate using a steel punch and die. The blank was about 2mm shorter in length and breadth than the article to be manufactured, and had the same volume as the article. The blank was heated in an over to 370°C under a blanket of nitrogen to prevent oxidative degradation, and was then quickly transferred to the bottom half of an unheated mould suitable for moulding the article. The mould was made from a block of metal filled epoxy resin. The top half of the mould was immediately brought into place and the mould closed at 100mm s^{-1} with a force sufficient to provide a pressure of about 10 MPa on the blank. Pressing continued for 30 seconds. The mould was then opened, to reveal a warm but solid moulded article with excellent surface and edge filling, no surplus flash or unwanted voids, and no buckling or tearing of the carbon cloth in evidence.

2. A second identical blank was cut from the laminate and the method repeated with a mould cycle time of 15 seconds. The quality of the article produced was found to be identical to that produced with a mould cycle time of 30 seconds.

CLAIMS

1. A fibre reinforced thermoplastics laminate comprising two or more reinforcing layers, each layer comprising a first thermoplastics material containing reinforcing fibres and, disposed between adjacent reinforcing layers, a thermoplastics layer comprising a second thermoplastics material wherein the first and second thermoplastics materials are the same or different and further wherein the ratio of the thickness of the thermoplastics layer to the thickness of each of the adjacent reinforcing layers is between 9 to 1 and 1 to 4.5.

2. A laminate according to Claim 1, wherein the ratio of the thickness of the thermoplastics layer to the thickness of each of the adjacent reinforcing layers is between 3 to 1 and 4 to 3.

3. A laminate according to either Claim 1 or Claim 2 wherein the first and second thermoplastics materials are different and are chosen such that, above the softening point of both materials and within a temperature range at which both materials exhibit fluid properties, at any one temperature within that range the viscosity of the first thermoplastics material is greater than the viscosity of the second thermoplastics material.

4. A laminate according to any one of the preceding claims wherein the two or more reinforcing layers comprise from 40% to 65% by volume of reinforcing fibres and from 60% to 35% by volume of the first thermoplastics material.

5. A laminate according to any one of the preceding claims wherein the reinforcing fibres are aligned in each of the reinforcing layers in the form of at least one triangulated net, crossply mat, continuous unidirectional mat or discontinuous unidirectional mat.

6. A laminate according to any one of the preceding claims wherein the reinforcing fibres comprise carbon fibres, glass fibres, asbestos fibres or aramid fibres.

7. A laminate according to any one of the preceding claims wherein thermoplastics layer comprises up to 30% volume of short fibres.

8. A laminate according to Claim 7 wherein the thermoplastics layer comprises from 2% to 15% by volume of short fibres.

9. A laminate according to either Claim 7 or Claim 8 wherein the average length of the short fibres in the thermoplastics layer is less than the thickness of said layer.

10. A laminate according to either Claim 7 or Claim 8 wherein the average length of the short fibres is between 0.1 and 1.0 mm.

11. A laminate according to any of Claims 7 to 10 wherein the short fibres comprise carbon fibres, glass fibres, asbestos fibres or aramid fibres.

12. A laminate according to any one of the preceding claims additionally comprising outer layers of a third thermoplastics material.

13. A fibre reinforced thermoplastics laminate substantially as hereinbefore described with particular reference to the Example.

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